Study on Degradation of Solid Oxide Cells during Electrolysis and Co-Electrolysis Operation

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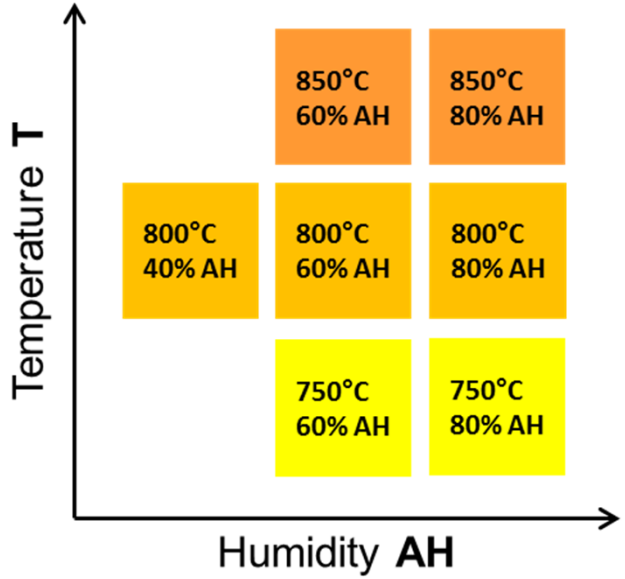
Outline

- Motivation and concept
- Degradation study on steam electrolysis
  - Test runs over 1000 hours under different conditions (i, T, humidity)
  - Impedance data and interpretation
  - Results from post-mortem analyses
- Degradation study on co-electrolysis: first results
- Conclusion

Systematic Study on Steam Electrolysis

Operating parameter → Degradation behavior

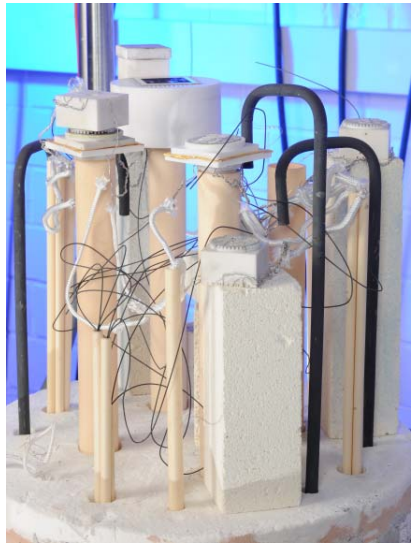
- Temperature (T): 750, 800, 850 ° C
- Fuel gas humidity (AH): 40%, 60%, 80% AH
- Current density (i): OCV, 0.5 A/cm^2, 1.0 A/cm^2, 1.5 A/cm^2



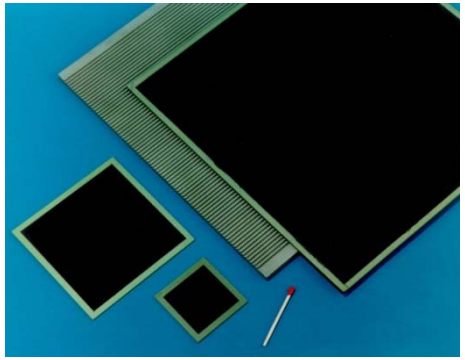
Systematic Study on Steam Electrolysis

Experimental concept:

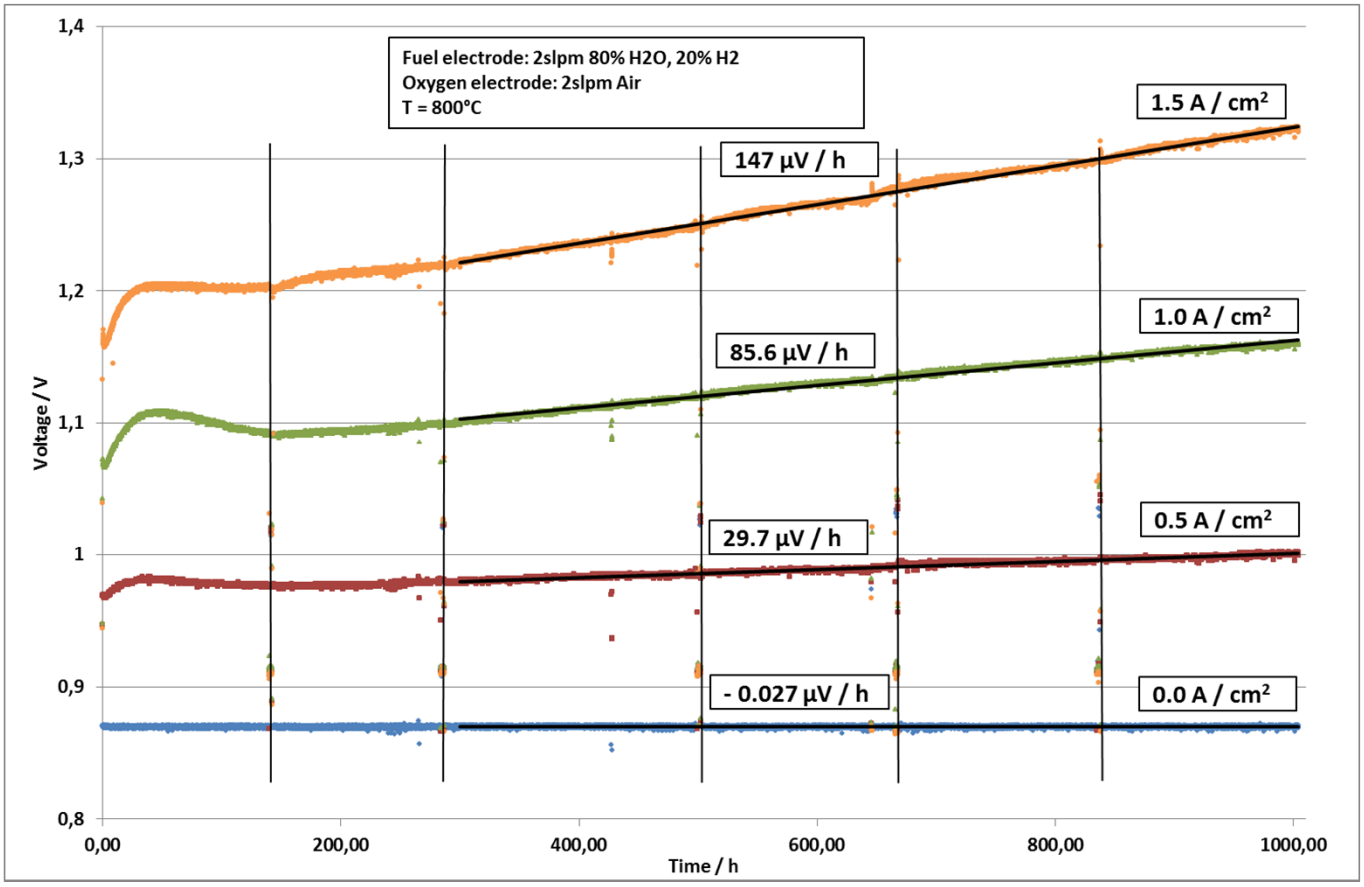
- Degradation experiments for 1000 h
- Test rig - quadruple cell measurement
  → Identical temperature, gas supply
  → Four different current densities simultaneously



- Fuel electrode supported cells from FZ Jülich and CeramTec Germany (16 cm^2)
  → Ni-8YSZ support | Ni-8YSZ | 8YSZ | CGO | LSCF



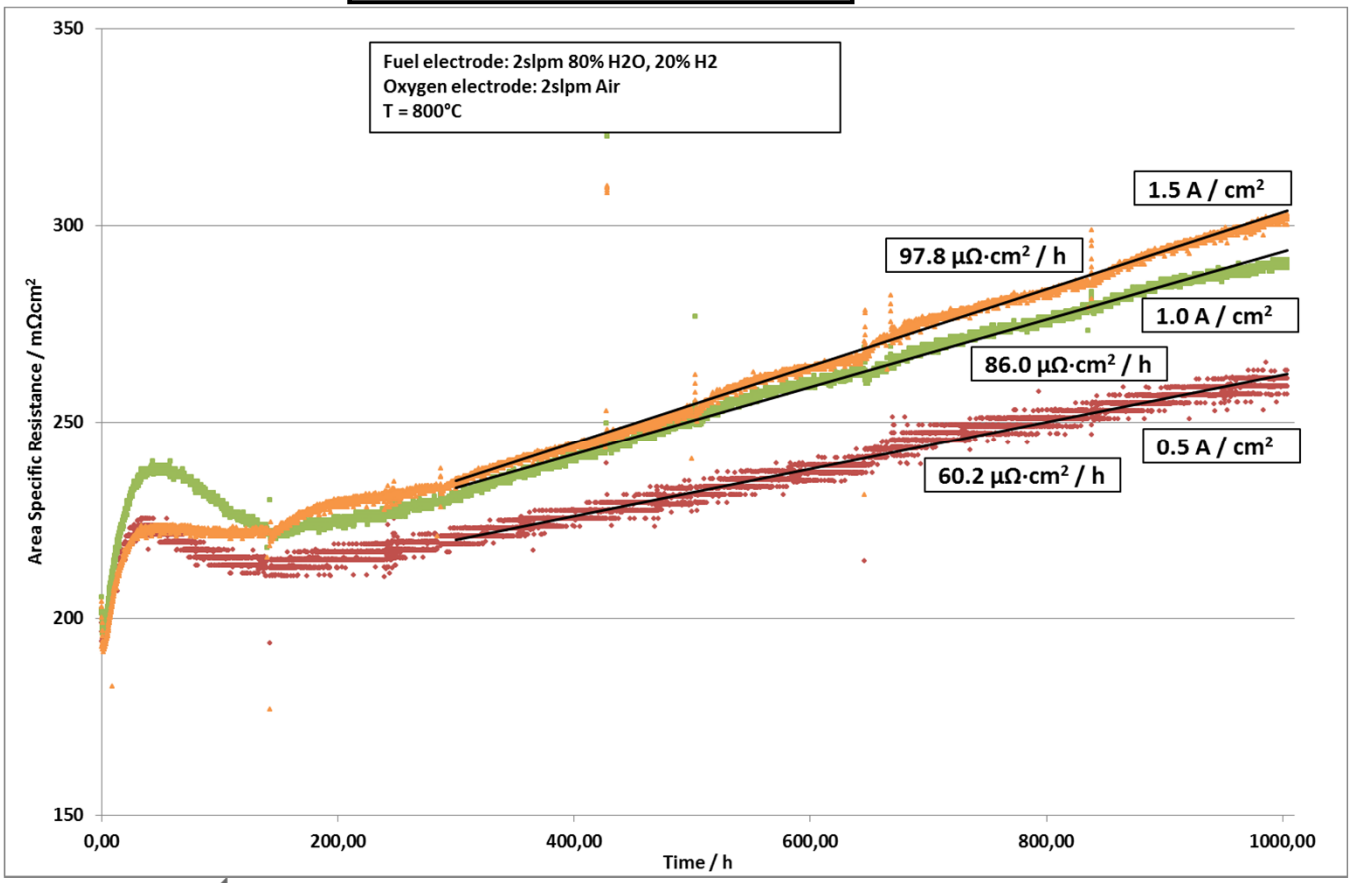
Degradation Experiment and Impedance Data Interpretation



- 4 cells measured simultaneously at different current densities
- Linear degradation after initial phase
- Be careful with interpretation of voltage degradation rate

Degradation Experiment and Impedance Data Interpretation

$$ASR(t) = \frac{U(t) - OCV}{i(t)}$$

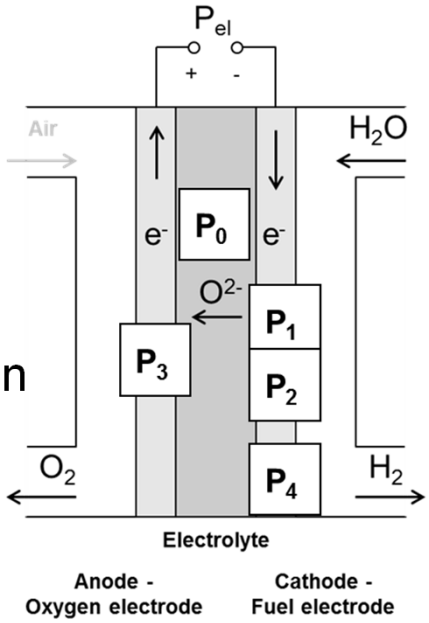


- Degradation rate at 1.5 A/cm^2 only 13 % higher than at 1.0 A/cm^2
- Degradation rate at 0.5 A/cm^2 significantly lower
- ASR degradation rate about 30% compared to 3% voltage degradation (per 1000 h @ 0.5 A/cm^2)

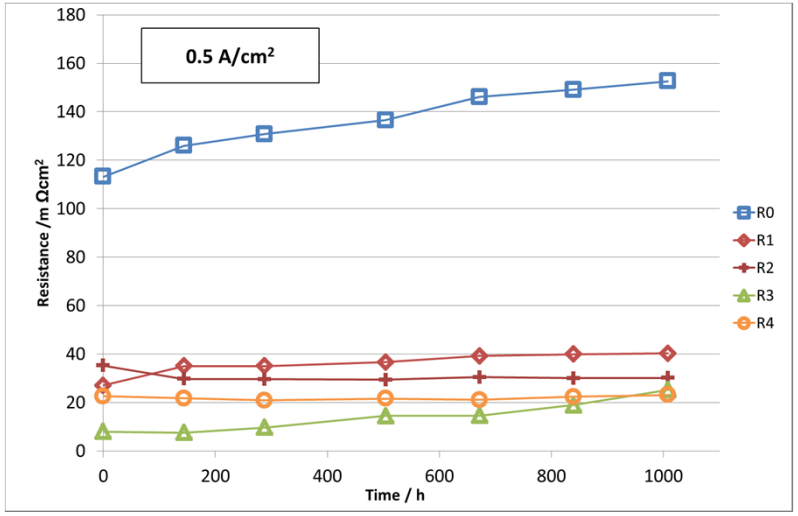
Degradation Experiment and Impedance Data Interpretation

Impedance data revealed 5 rate limiting processes:

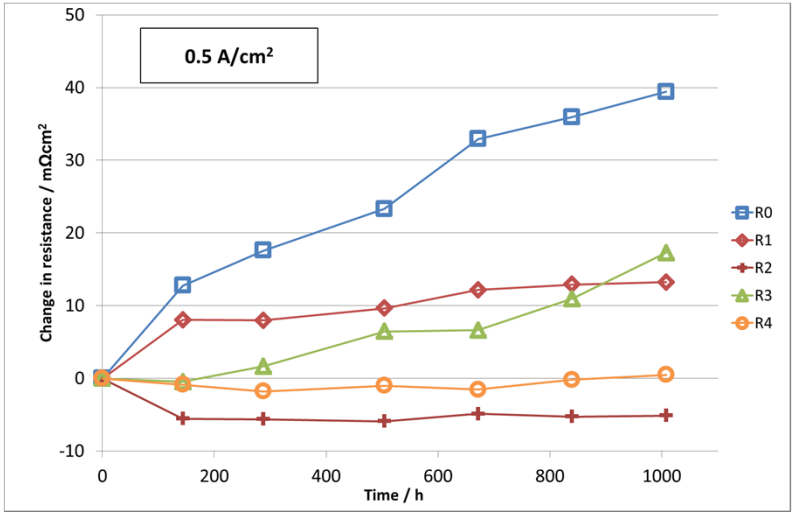
- P_0: Ohmic resistance (> 10^5 Hz)
- P_1: Fuel electrode process A (~ 10^4 Hz)
  Charge transfer reaction at TPB coupled with ionic transport in porous electrode geometry
- P_2: Fuel electrode process B (~ 10^3 Hz)
  Charge transfer at TPB
- P_3: Oxygen Electrode Process (~ 10^2 Hz)
- P_4: Fuel electrode mass transport limitation (~ 10^1 Hz)
  Diffusion through FE-support along with gas conversion



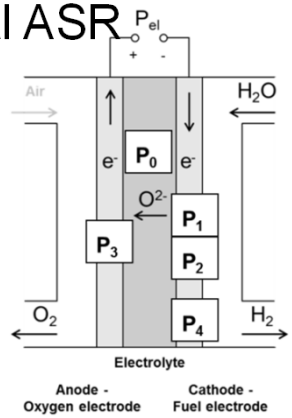
Influence of Current Density on Degradation



ΔR

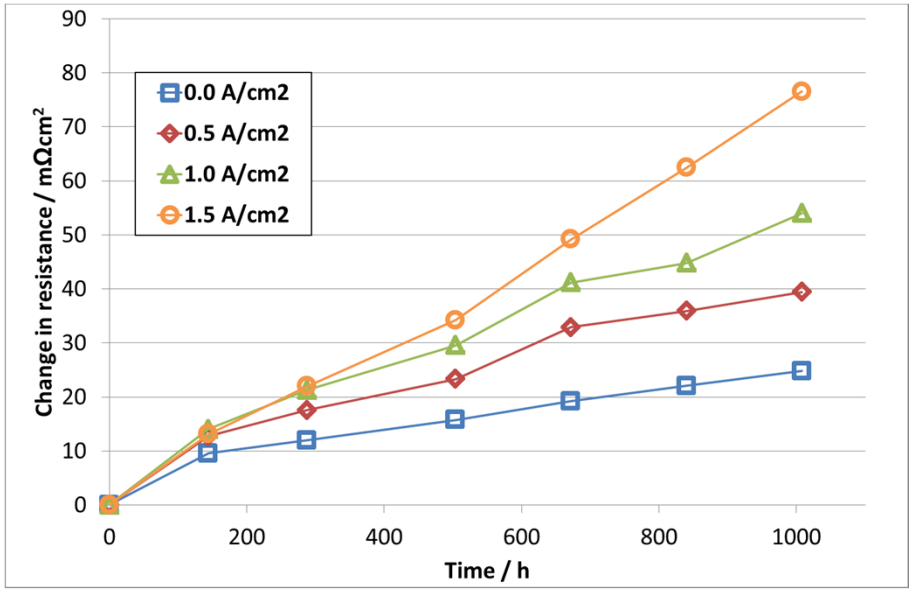


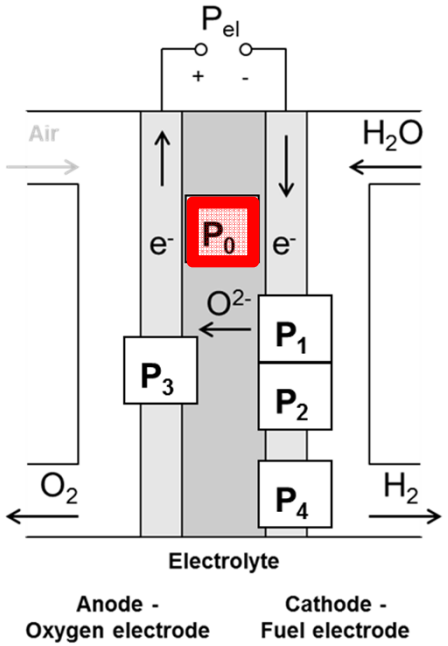
- Ohmic resistance contributes more than 50% of total ASR



- Degradation of ohmic resistance is most severe
- Oxygen electrode has small ASR but high contribution to degradation
- Fuel electrode process 1 degrades while process 2 improves performance

Influence of Current Density on Degradation

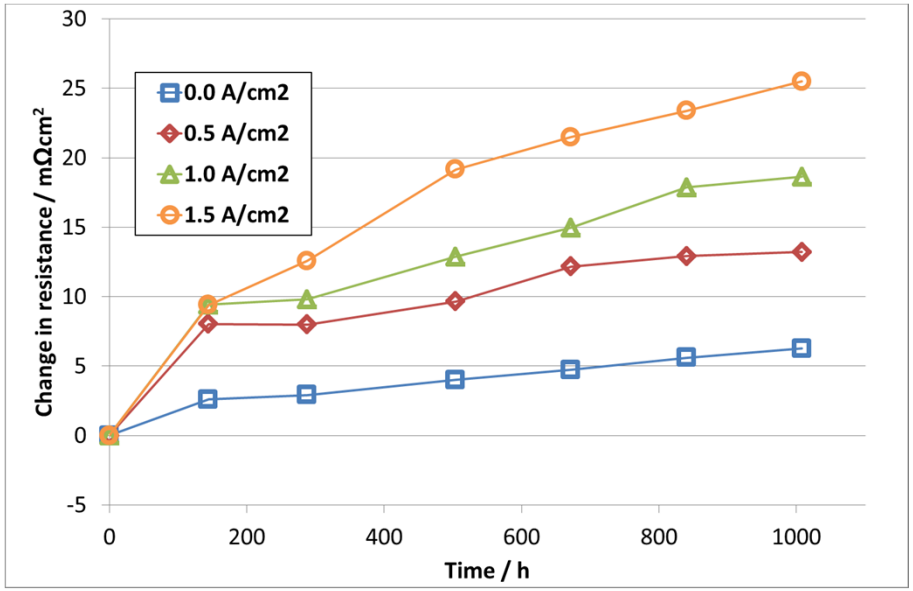


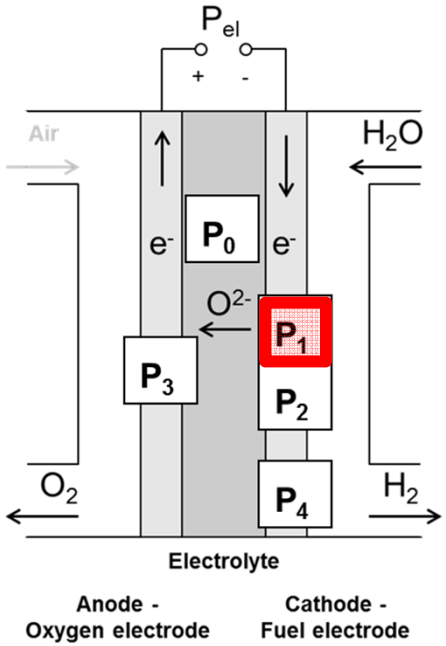


P_0: Ohmic resistance

- Obvious correlation with current density
- Linear degradation with time

Influence of Current Density on Degradation

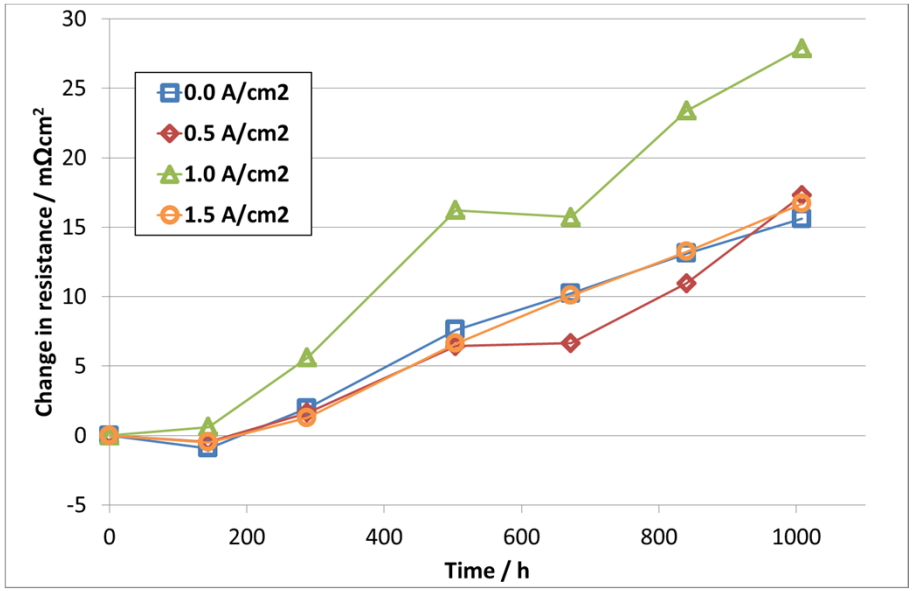


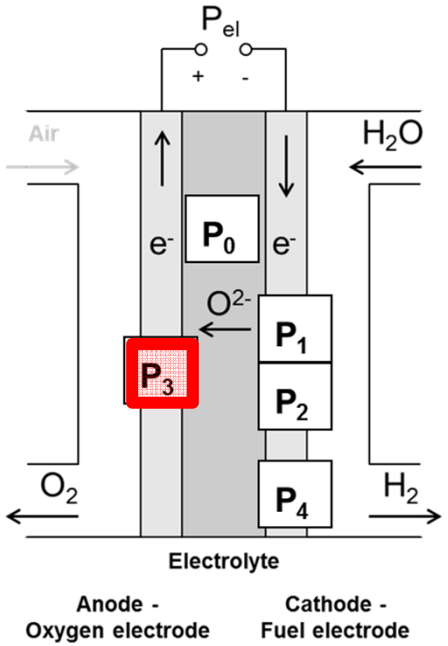


P_1: Fuel electrode process

- Also obvious correlation with current density
- Degradation initially fast but slowing down with time

Influence of Current Density on Degradation

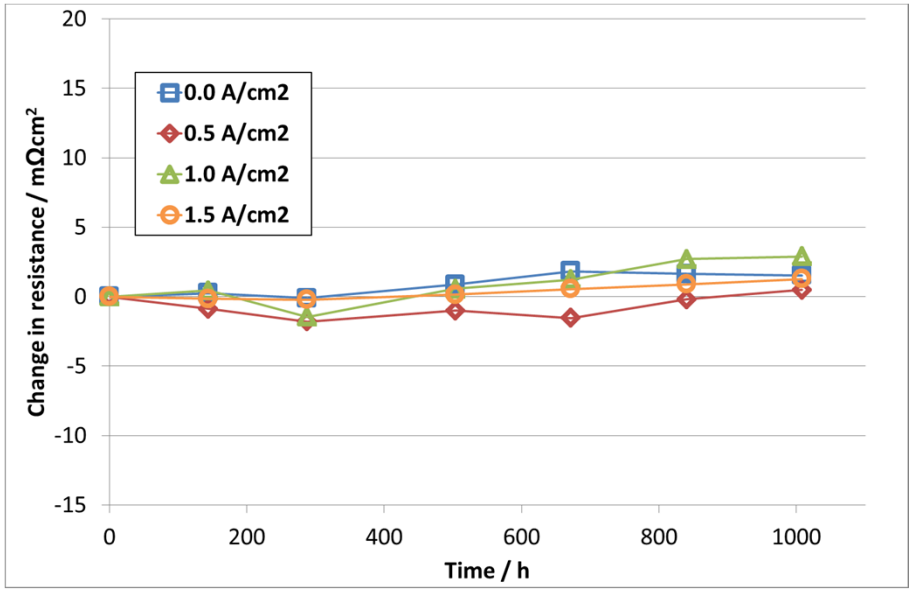


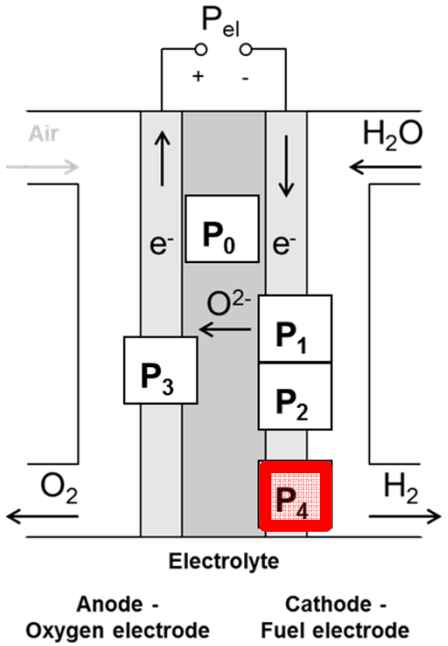


P_3: Oxygen electrode process

- Shift shown by 1.0 A/cm^2 curve is likely artifact
- Initially stable → afterwards linear degradation
- Degradation independent of current density

Influence of Current Density on Degradation





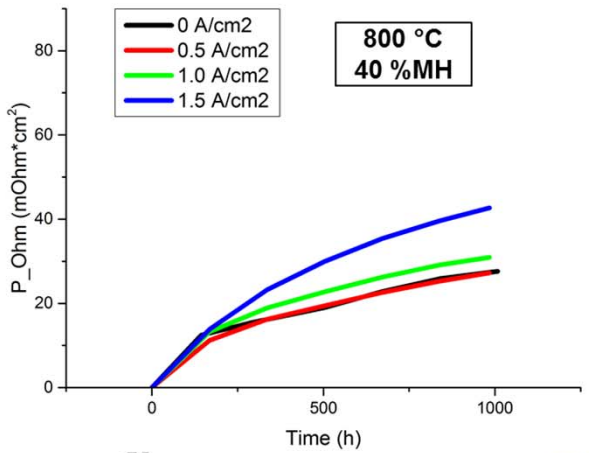
P_4: Fuel electrode mass transport

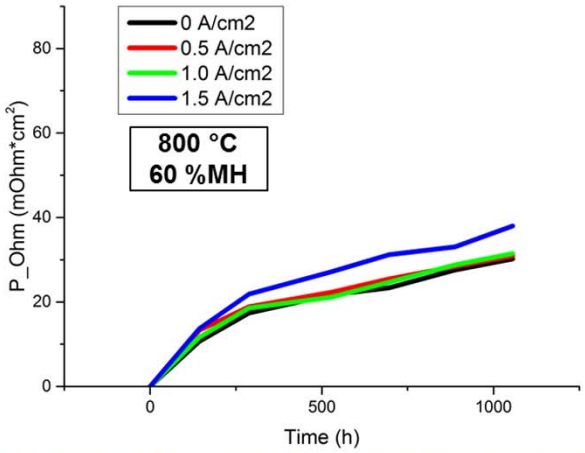
- Very little degradation
- Independent of current density

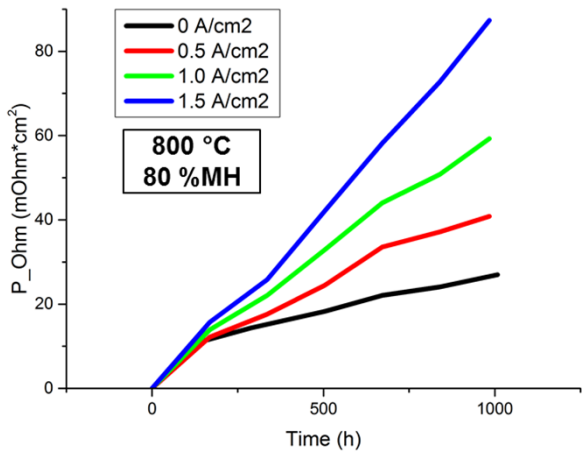
Degradation Results: Ohmic Resistance

40 % MH and 60 % MH	80 % MH
▪ Degradation of ohmic resistance at all current densities	▪ Influence of current density much stronger
▪ Influence of current density only at high current densities	▪ Current density has effect even at low current densities

Degradation caused by a combination of current density and high humidity

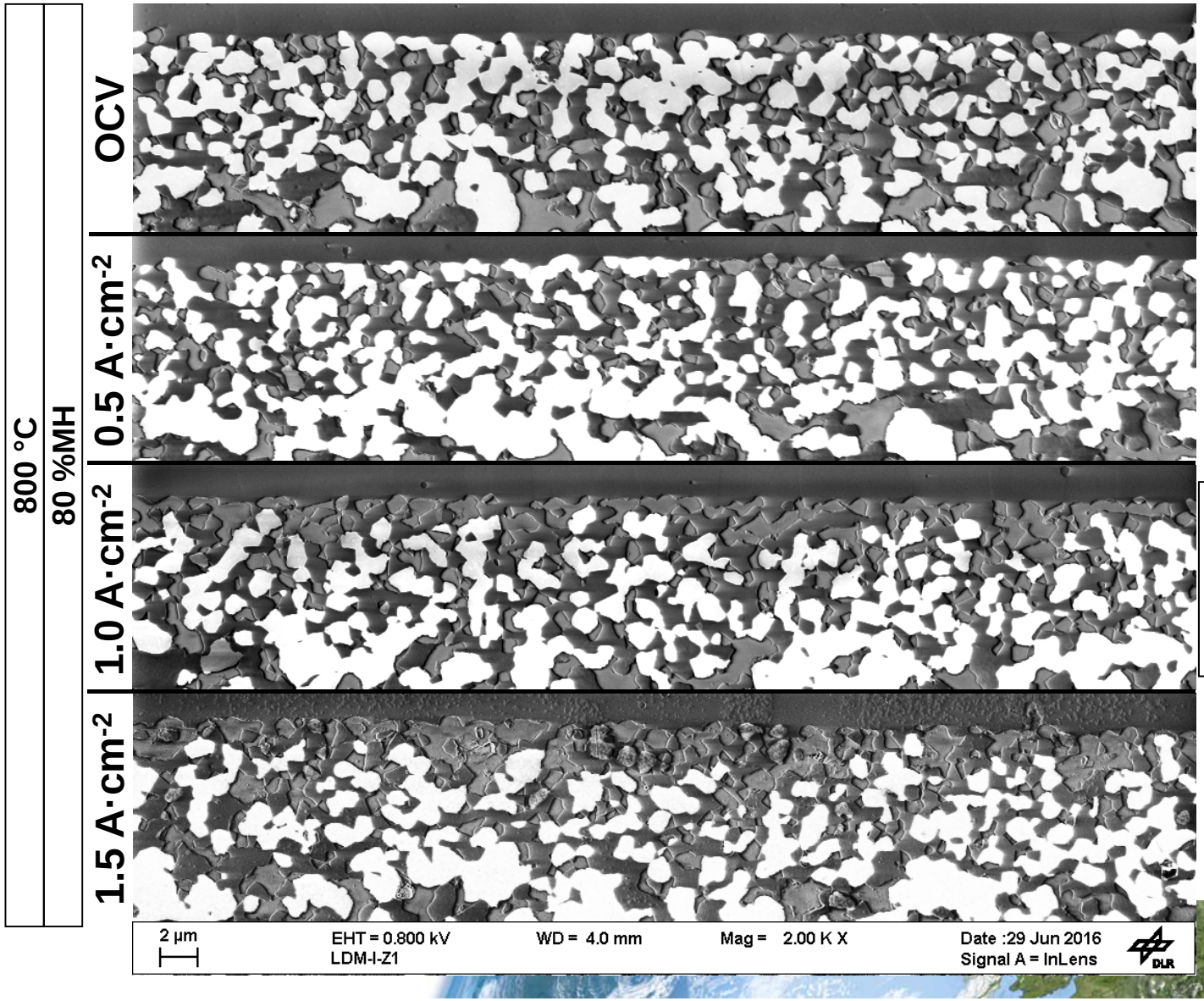






DLR

Degradation Results: Ohmic Resistance

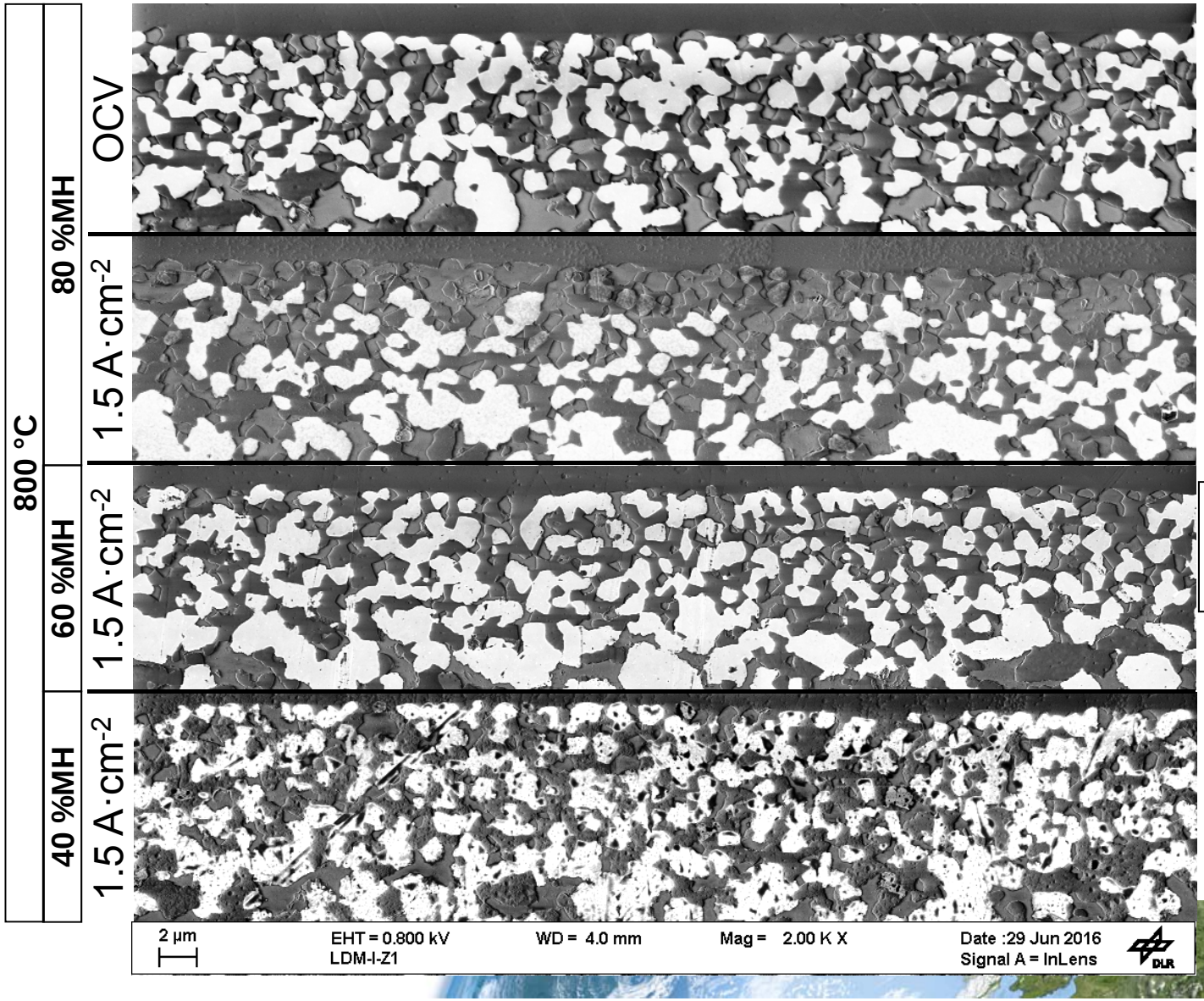


Ni depletion at electrode|electrolyte interface

→ Effectively increasing electrolyte thickness

Direct correlation between Ni depletion and current density

Degradation Results: Ohmic Resistance

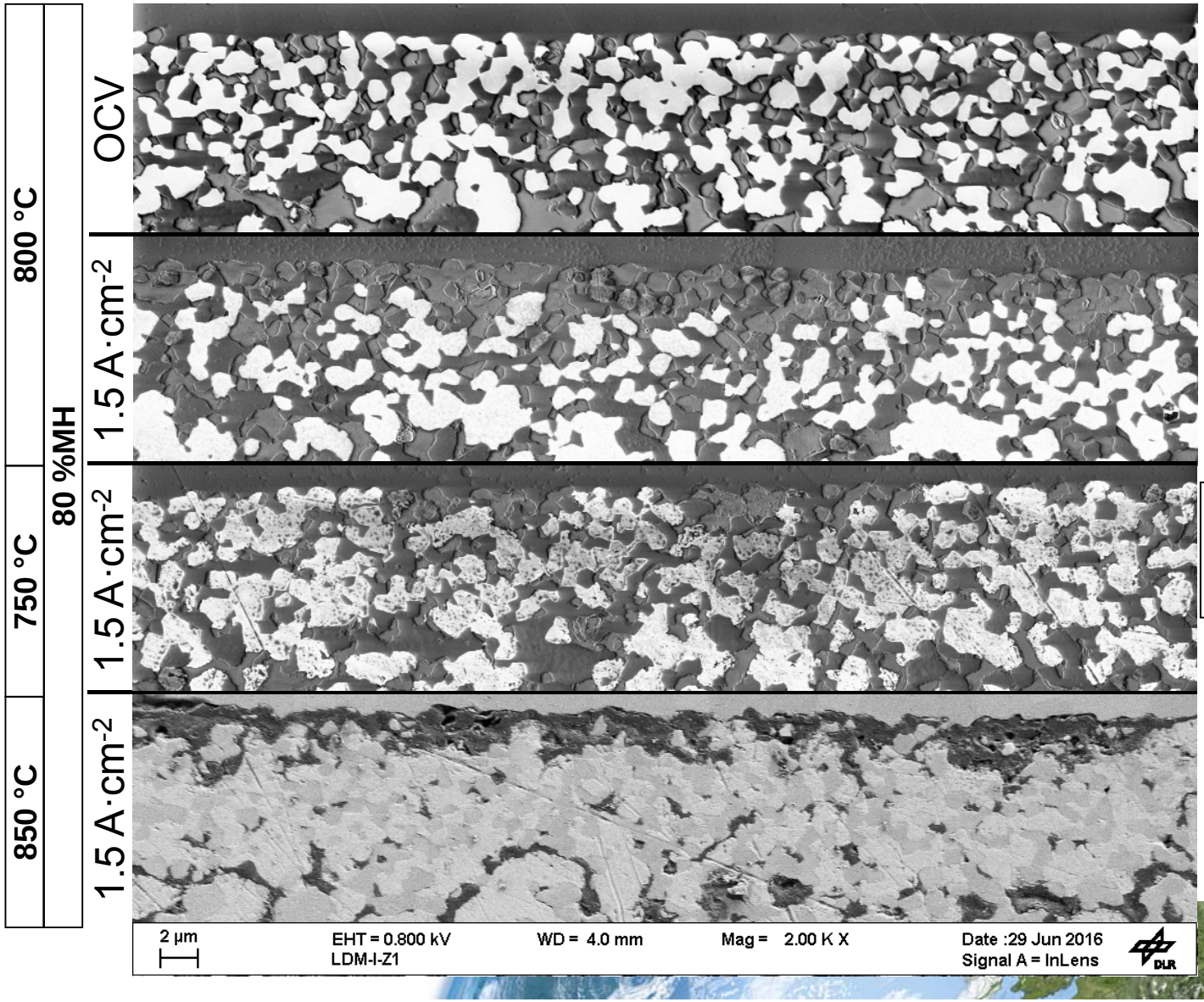


Ni depletion at electrode|electrolyte interface

→ Effectively increasing electrolyte thickness

No Ni depletion at lower humidity

Degradation Results: Ohmic Resistance



Ni depletion at electrode|electrolyte interface

→ Effectively increasing electrolyte thickness

Less Ni depletion at lower temperature

Degradation Results: Ohmic Resistance - Summary

Two major degradation processes

Ni Depletion:

- Direct correlation between current density and Ni depletion
- Minimum humidity (above 60 %MH) required
- Temperature facilitates process

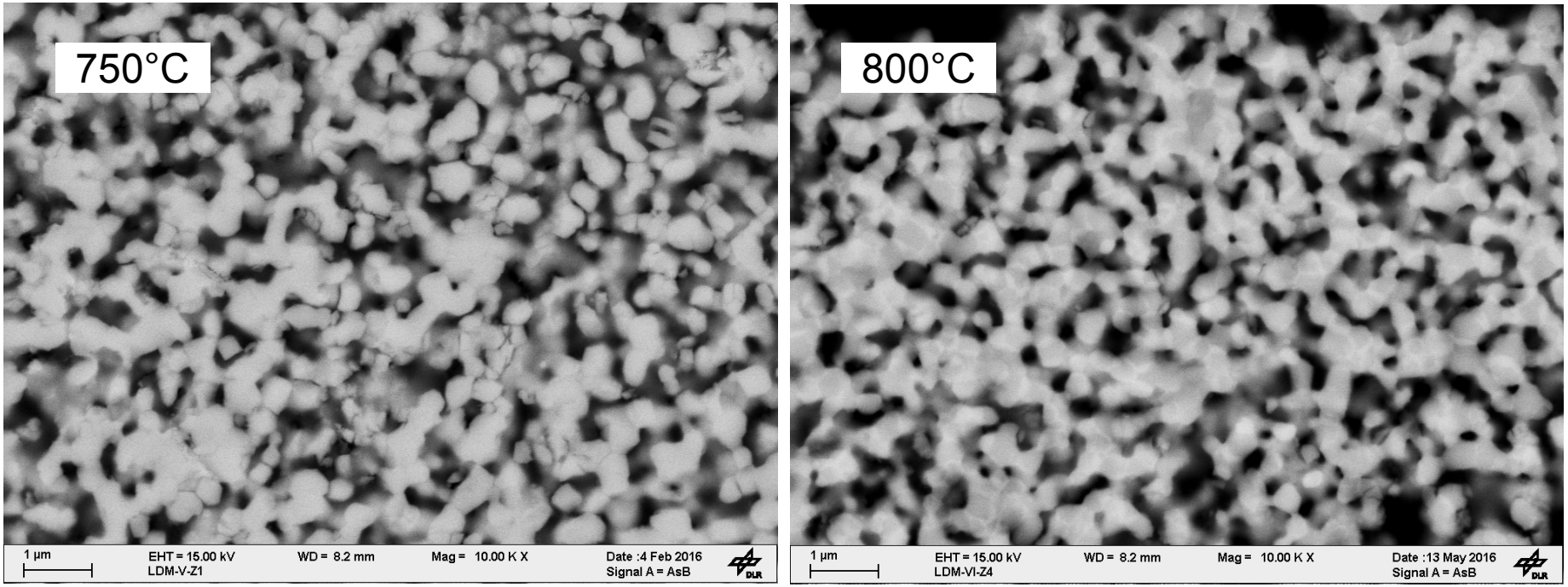
Deterioration of YSZ integrity

- Weakening of YSZ structure at high current densities

Not observed

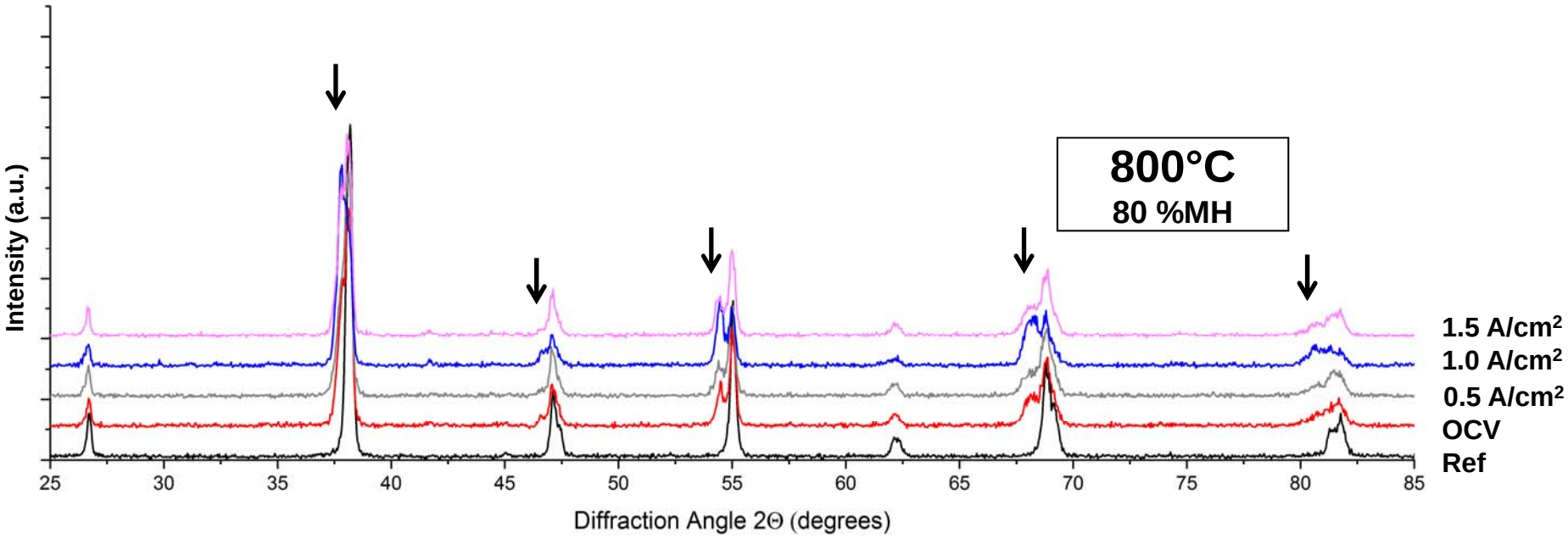
- Correlation between YSZ deterioration and significant increase in ohmic resistance
- $SrZrO_3$ formation

Degradation Results: Oxygen Electrode



- Change in phase composition observable in BSE-SEM
- Correlates with new peaks on XRD pattern
- Correlates with degradation of electrochemical activity

Degradation Results: Oxygen Electrode



- New peaks in XRD patterns → suggest formation of new crystalline phase
- Observable at all current densities, but no clear trend
- Similar at 800 °C and 850 °C

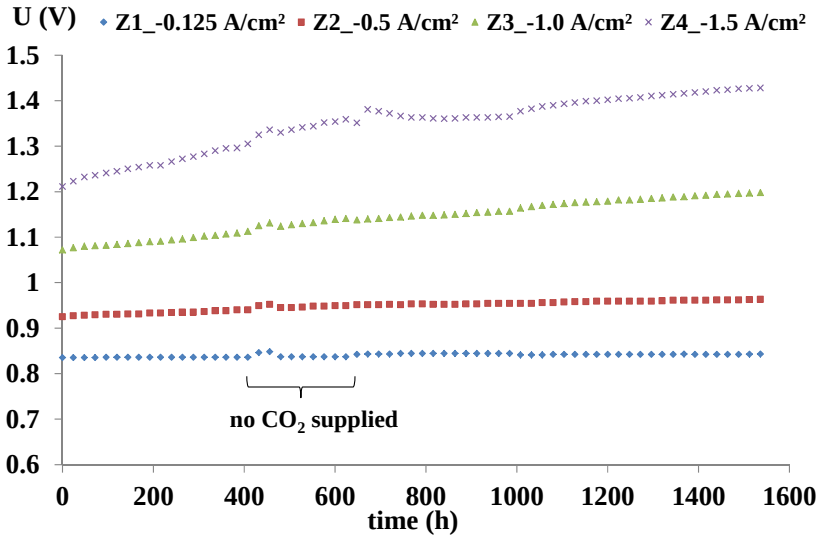
Co-electrolysis Operation over 1500 hours

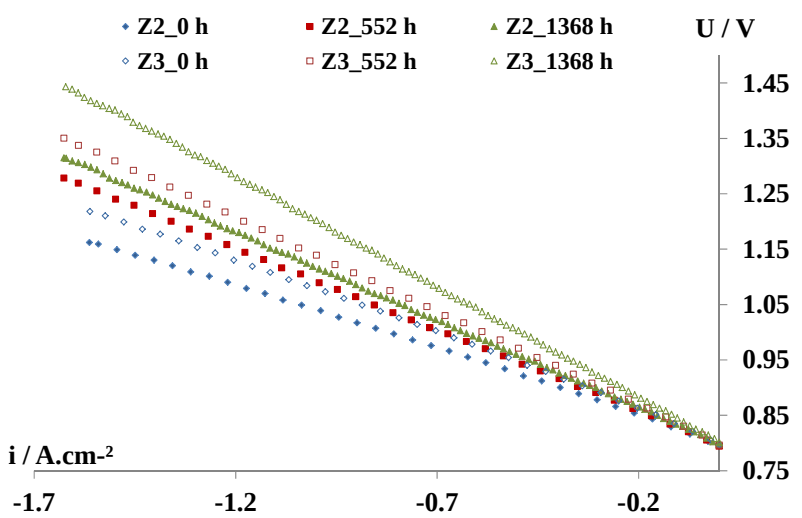
Fuel electrode supported cell: CeramTec, Germany

Operating conditions:

Fuel electrode: 57% H_2O + 36% CO_2 + 7% H_2; oxygen electrode: O_2 ; T = 800°C,

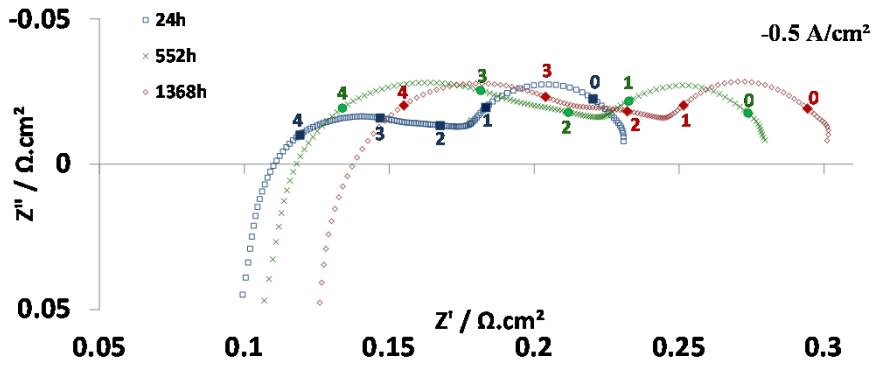
H_2 electrode flow rate = 0.7 SL/min/cell, O_2 electrode flow rate = 2.0 SL/min/cell

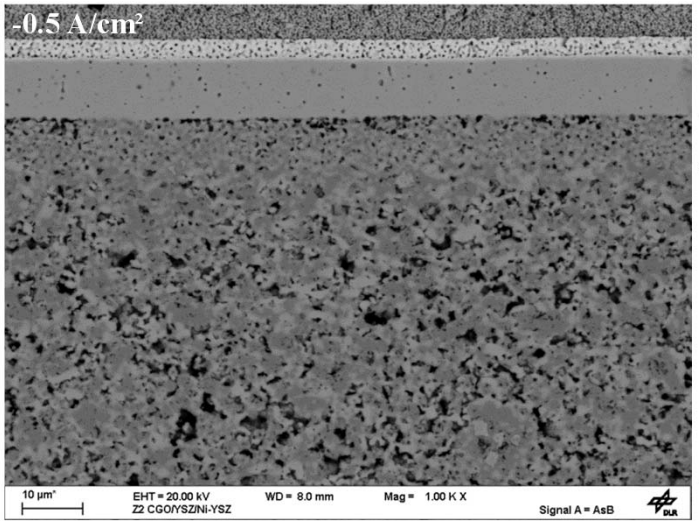


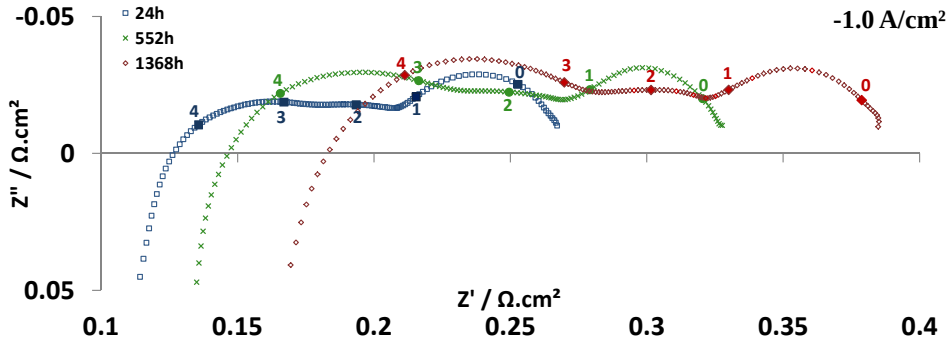


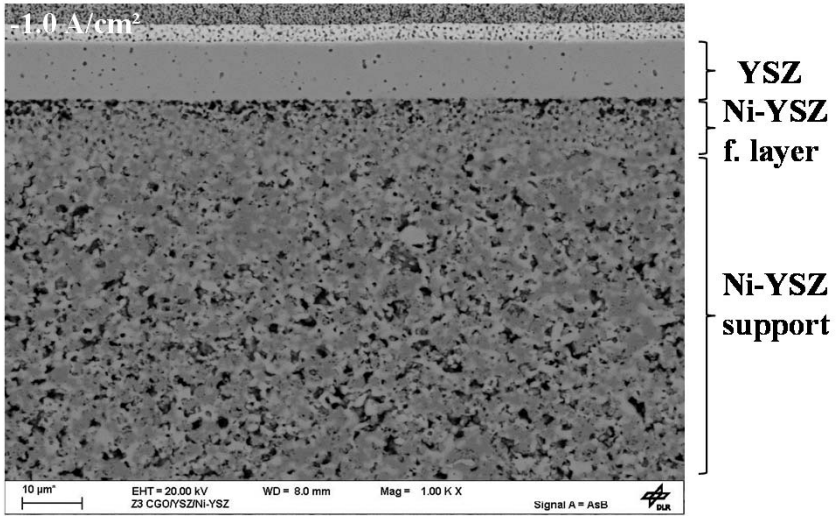
1536 h Test	Z1	Z2	Z3	Z4
ΔV (mV/1000 h)	5.2	24.7	82	141
%/1000 h	0.6	**2.7**	**7.7**	**11.7**

Co-electrolysis Operation over 1500 hours









Ni depletion !

Summary

Steam electrolysis: Correlation between degradation and operating conditions such as current density, temperature and humidity has been investigated

- Ohmic degradation dominates overall degradation and increases with current density
- Major ohmic degradation process:
  - Ni depletion: f(i) above T and humidity threshold
- Changes in the oxygen electrode:
  - Oxygen electrode contributes to degradation and is independent of current density
  - XRD and BSE-SEM images show change of phase composition
  - Correlates with degradation of electrochemical activity
- Fuel electrode degradation:
  - Stronger at higher current densities
  - Ni agglomeration at high T

Co-electrolysis:

- In co-electrolysis operation similar trend for the fuel electrode is observed as in steam electrolysis.
- Higher degradation might occur under co-electrolysis conditions, e.g. due to CO_2 electrolysis

Acknowledgment

I‘d like to thank my PhD student Michael Hörlein and Dr. Aziz Nechache for their scientific work and strong effort.

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Thank you for your attention